

Compositional Analysis by Energy Dispersive X-Ray Fluorescence Spectrometry (EDXRF)

1 Introduction

Energy dispersive x-ray fluorescence spectrometry (EDXRF) is a technique that can be used for the non-destructive elemental analysis of a wide variety of materials for elements ranging in atomic number from fluorine to uranium. Microspot EDXRF is used for the analysis of specimens that are too small for standard x-ray fluorescence analysis methods. Both EDXRF and microspot EDXRF can be used to characterize the major, minor, and trace elemental constituents present in solid and liquid specimens.

2 Scope

This document applies to personnel using the associated instrument(s)/equipment in support of metallurgy, anthropology, polymeric, or general chemistry examinations. This procedure serves as a general guideline for all FBI Laboratory procedures that use EDXRF.

Application of this SOP to evidentiary materials requires knowledge of general concepts of x-ray fluorescence spectrometry analysis. Methods requiring analysis by EDXRF require operational proficiency of each instrument employed. This knowledge can be obtained from the references provided, training from manufacturers or principal operators, or schools covering theory or instrument operation.

General procedures for compositional analysis by EDXRF and microspot EDXRF are described below. Operational procedures for specific instruments are detailed in supplemental SOPs. (See References section.)

3 Principle

EDXRF has its basis in quantum mechanics. An incident x-ray beam is used to eject core electrons from the atoms comprising the sample. Subsequent relaxation from the excited state results in emission of x-ray photons (x-rays), each with an energy that is characteristic of the element emitting it. Each photon striking the detector generates an electronic reaction that is converted to a digital signal which is processed to determine the energy of the incident photon. Many such emission and collection events are measured during a single experiment. The spectral output is a histogram displaying the number of photons (or “intensity”) collected at each energy level over the time interval of the test. The energies of the detected peaks provide information about the elements present in a specimen, while the relative intensities of the peaks allow the concentrations of each element to be determined.

Microspot EDXRF is a modification of standard EDXRF in which the x-ray beam is focused down to a small spot size. This is accomplished using a beam collimator or a poly-capillary or mono-capillary x-ray lens. Such configurations permit elemental analysis of specimens as small as the incident spot size.

4 Specimens

Liquid and solid substances can be analyzed by this method. Particles as small as 50 μm in diameter can be examined using microspot EDXRF. Since the incident x-rays will interact with the specimen surface, any surface coating or contamination will be irradiated during the procedure and might contribute to the measured spectrum. Specimens may need to be cleaned or ground to measure underlying layers or base material.

For quantitative analysis, specimens must be prepared so that they have a flat, smooth surface and be sufficiently thick to accommodate the entire x-ray interaction volume.

For liquids or fine powders, a plastic cup can be used to contain the specimen. Depending on the orientation of the x-ray tube and detector, either the flat surface of the specimen will provide the required analysis surface or the specimen will be measured through a layer of polymer film.

5 Equipment/Materials/Reagents

- a. EDXRF spectrometer, such as:
 - Thermo QUANT'X X-ray Fluorescence Spectrometer
 - Bruker M4 Tornado Micro X-ray Fluorescence Spectrometer
 - Olympus Delta Premium Handheld X-ray Fluorescence Spectrometer

The choice of instrument to use will depend on the desired measurement environment, the available amount and particle size of the specimen, and the elements to be measured. Each EDXRF instrument has different capabilities to measure major and minor alloying elements and trace elements in different matrices. Refer to the individual instrument SOP for known limitations.

- b. Performance check standard(s) appropriate for the specific instrument used.
- c. Mounting materials (optional, depending on specimen) such as:
 - Graphite stubs
 - Durotak mounting adhesive
 - Plastic specimen cups (for liquids or powders)
 - Chemplex X-Ray Mylar (2.5 μm thick) or Polypropylene film (6.3 μm thick) or similar

- d. Reference materials of alloys similar to the type(s) under analysis for alloy grade determination
- e. Certified reference materials (CRMs) of alloys similar to the type(s) under analysis for elemental quantitation or establishing limit of detection (LOD)

6 Standards and Controls

Reference materials are often used to demonstrate the discernment of major, minor, and trace elements in alloys similar to the specimen under the same measurement conditions. Quantitative analyses will be appropriately validated using CRMs.

EDXRF instruments are not calibrated by instrument operators. Adequate instrument performance is demonstrated prior to case work by performing a verification or energy adjustment routine. The required performance check standard is listed in each instrument SOP. At a minimum, a performance check is completed each day prior to the instrument being used for case work. In addition, energy adjustment will be performed when the spectrum peaks become shifted from their theoretical energy positions by more than 0.05 keV. A record of the performance check is retained near the instrument, in either electronic or paper form, to track historical performance.

7 Sampling

Refer to the specific case work SOP(s) for appropriate sampling procedures (e.g., *Examinations for Association and Origin* for metallurgy examinations.)

For bulk analysis of small particulate matter (like soil or fines), the material must be mixed until it appears visually homogeneous before extracting a specimen.

8 Procedure

8.1 Basic Operation

The basic operation of each individual instrument is detailed in the instrument SOP. The general steps for performing EDXRF analysis follow:

- a. Run the instrument performance check routine. File one copy with the instrument performance records.
- b. Prepare and insert the specimen(s).
- c. Apply the desired atmospheric environment: air, helium, or vacuum. Do not perform evacuation on unconstrained fine powders or on liquids. Fine powder can be protected from disseminating under vacuum if contained in a specimen cup with a perforated film cover.
 - i. To detect low atomic number (low Z) elements such as sodium and silicon, specimens are typically analyzed under vacuum of 1 torr or less (standard atmospheric pressure is 760 torr). This optimizes the detection limits of low Z elements by eliminating the attenuation of low energy fluorescent x-rays in air. Analyzing under vacuum also eliminates spectrum interference by argon x-ray fluorescence which occurs as the x-rays pass through air.
 - ii. Helium is useful for measuring low Z elements in liquids because it is a poor x-ray absorber and does not contribute interfering signal.
 - iii. For specimens where evacuation is not possible (e.g., fine powder or liquid), analysis will be conducted in air or helium atmosphere.
 - iv. For specimens where low Z elements (F through Ca) are not present or relevant, analysis in air is acceptable.
- d. Adjust instrument conditions to best reveal the analytes (elements) of interest. This may be an iterative process. Selection of x-ray tube voltage and filtering is dependent upon the specimen composition and the objective of the analysis. Choice of the optimal conditions for a given analysis requires experience and a basic knowledge of x-ray physics. Suitable tube current is dictated primarily by the need to have a sufficient count rate to collect a spectrum.
 - i. If the compositions of two specimens are to be compared, analyze them both under the same instrumental conditions.
 - ii. If a specimen is to be compared to an alloy class or classes, analyze appropriate reference materials under the same instrumental conditions as the unknown specimen.
 - iii. If the absence of an analyte is under consideration, establish a limit of detection (LOD) for that analyte in a similar matrix under the same instrumental conditions.
 - iv. If quantitative compositions are to be reported, appropriately validate the analytes

of interest in a similar matrix using CRMs.

- e. Acquisition duration will depend on the conditions chosen and the specimen area exposed to the incident beam, but must be adequate to acquire sufficient counts for analysis. The acquisition time can be extended to optimize spectrum clarity or shortened to enhance collection efficiency based on the requirements of the case.
- f. Ensure the instrument identification and the operating parameters are recorded on the printed spectra or elsewhere in the case notes.

8.2 Spectral Analysis

Determination of the elements detected in a spectrum requires analysis of peak shapes, energies, and the relative heights of adjacent peaks, and consideration of the effects of secondary and tertiary fluorescence, and other x-ray/specimen interactions. System peaks, sum and escape peaks, Rayleigh and Compton scattering, and diffraction may also contribute peaks to the spectrum and should be considered when interpreting spectra. Some EDXRF systems have software that can accurately identify the escape and sum peaks in a spectrum. The peak identification system resident in the instrument software can be augmented by analyzing reference materials of similar composition to the specimen of interest.

8.3 Quantitation of Data

In general, x-ray spectra are not used to generate quantitative data. However, the spectra acquired from a specimen can be processed to yield weight concentrations of the elements detected. Different EDXRF instruments employ different software routines to quantitatively process spectral data. If numerical compositional data is to be reported, validation must be performed on the same instrument under the same operating conditions using CRMs with a matrix similar to that of the specimen of interest.

9 Instrumental Conditions

Instrument conditions will vary depending on the instrument and application. See the Basic Operation section and individual instrument SOPs.

10 Decision Criteria

10.1 Instrument Performance

Instrument performance is demonstrated during the instrument performance check.

During analysis, energy adjustment of the instrument will be undertaken whenever the measured x-ray peak positions differ by more than 0.05 keV from their theoretical positions.

10.2 Qualitative Analysis

Peak identification on EDXRF spectra requires a thorough understanding of x-ray physics, instrument performance and potential artifacts. Although instruments provide peak identification software, the analyst is required to interpret the validity of the suggestions produced by programs using libraries of x-ray energy lines. In addition:

- a. Comparisons between specimens must consider possible surface or embedded contamination, variations in surface topography between specimens and any variation in the as-manufactured homogeneity of pristine specimens.
- b. Comparison to an alloy class or classes must consider the factors above and the possibility of overlapping compositions among alloy classes. Although it may be possible to demonstrate that a specimen is of similar composition to a particular alloy class, it may be impossible for EDXRF to reveal whether a material was produced to a particular specification.
- c. If the absence of an analyte is under consideration, the LOD for that analyte in a similar matrix under the same instrumental conditions will be estimated or validated as appropriate.

10.3 Quantitative Analysis

If quantitative compositions are to be reported, a CRM (selected by alloy) is used to check the accuracy of the quantitative analytical results produced by the validated method (see the Quantitation of Data section). If the measured concentrations of the major elements of interest deviate by more than 15% from the certified values, the analysis will be rerun as systematic errors may be present. In some materials, element peaks of a minor constituent may be overlapped by a major constituent rendering the former indistinguishable. For example, the manganese peaks in stainless steel alloys are masked by those of chromium and iron. In such instances, any concentration results generated for the overlapped, minor constituent element will be regarded as qualitative in nature.

11 Calculations

Calculations for establishing relative concentrations of elements in a measured specimen are embedded in quantitation software routines of each EDXRF instrument. The internal routines are verified by CRMs during the validation process.

The expected position of escape and sum peaks on the energy axis can be calculated if they are

not automatically generated by instrument software:

- a. For instruments using silicon-based detectors, an “escape peak” may appear at 1.740 keV less than the energy peaks of the major constituent(s).
- b. “Sum peaks” may appear at an energy equal to the sum of the peak energy(ies) of major constituent(s). For example, in a brass alloy with high zinc content, sum peaks can be seen at double the Cu K α energy, double the Zn K α energy and at the Cu K α + Zn K α energy.

12 Measurement Uncertainty

Typically, EDXRF is not used for quantitative analysis. In the event that it is necessary to estimate the measurement uncertainty of an instrumental result, it will be done in accord with the *Chemistry Unit Procedures for Estimating Measurement Uncertainty*.

13 Limitations

The physical interactions of incident and emitted x-rays with the different components of an x-ray measurement system, including the measured specimen, must be taken into account when analyzing EDXRF spectra:

- a. The detection limit of an element is dependent upon its atomic number, the matrix material, the analysis atmosphere, the presence of overlapping element energy peaks, acquisition time, any filters used and other factors. Parts per million (ppm) level detection limits are readily obtained in some situations. More commonly, the practical detection limits in metal alloys range from ~0.01 - 0.1 weight percent depending on the matrix and the element being analyzed.

Where required, specific detection limits under a given set of analytical conditions can be estimated by analysis of compositionally similar CRMs or other suitable positive controls (e.g., reference or known materials) containing known levels of the analyte of interest using identical instrumental conditions. The first eight elements of the periodic table (H, He, Li, Be, B, C, N, O) cannot be detected at any concentration by EDXRF systems that employ a beryllium detector window.

- b. Unusually thin specimens may result in skewing of the relative heights of the various energy peaks and thus cannot be reliably quantified. Similarly, a layered specimen may produce a spectrum containing signal from the multiple layers.
- c. Peak identification in a spectrum can be complicated by the presence of diffraction peaks, scatter peaks associated with the x-ray tube target material, and other system peaks as

discussed in the Spectral Analysis section. For example, using Mylar film to support a specimen may contribute a Ca peak to the spectrum. Organic matrices also generate high background scatter. Analyzing a known material with a matrix similar to the specimen can often help identify these artifact features in a spectrum.

- d. On-board peak identification routines compare measured energy intensities with the known characteristic energies emitted by elements. The analyst must take into account the likelihood of the presence of any particular element. For example, in a manganese standard, an automated peak identification routine may indicate that an energy peak at 6.49keV could be a Dy L α line or a Mn K β line. The analyst should recognize that dysprosium is not likely to be present based on its rarity in the earth and upon the absence of additional Dy spectral emissions.
- e. Different types of x-ray detectors have different limitations of performance. Solid state detectors using lithium-drifted silicon crystals (SiLi) require sufficient cooling to retain chip integrity and provide adequate energy resolution (e.g., Peltier cooling). Silicon drift detectors (SDD) do not need to be cooled as severely to achieve adequate resolution, but they provide relatively poor sensitivity for high energy x-rays. This effect can be mitigated somewhat by choosing optimum tube excitation and filtering conditions during measurement.
- f. X-ray fluorescence energy spectra are subject to numerous, but well documented, interferences from other element characteristic energies. The following common interferences are known for spectra collected using energy dispersive detectors. The presence of these interfering species can usually be determined from examination of the affected peak series, the peak height ratios and the presence of higher energy peaks that will normally accompany the interfering species.

Element	Interferences
F (K lines)	Fe (L lines)
Na (K lines)	Cu (L lines)
Mg (K lines)	As (L lines); Tb (M lines)
Al (K lines)	Br (L lines); Tm, Yb (M lines)
Si (K lines)	Rb (L lines); Sr, W (M lines)
P (K lines)	Zr (L lines); Ir (M lines)
S (K lines)	Mo (L lines); Pb (M lines)
Cl (K lines)	Rh (L lines); Ru (L lines)
K (K lines)	In (L lines)
Ca (K lines)	Te (L lines); Sb (L lines)
Ti (K lines)	V-K α ; Ba (L lines); La (L lines)
V-K β line	Cr-K α line
Cr-K β line	Mn-K α line

Mn-K _β line	Fe-K _α line
Fe-K _β line	Co-K _α line
Co-K _β line	Ni-K _α line
Ni-K _β line	Cu-K _α line
Cu-K _β line	Zn-K _α line
As (K lines)	Pb (L lines)

14 Safety

- a. Wear an x-ray film badge or dosimeter when operating instruments that generate x-rays. The instruments have protective enclosures and internal safety interlocks to prevent inadvertent x-ray radiation exposure. Never bypass or disable safety interlocks on instruments.
- b. Some EDXRF detector windows are comprised of beryllium and are extremely delicate. In the event of damage to a beryllium window, the beryllium dust created could pose an acute health hazard. If this occurs, seal the chamber and seek assistance from the Laboratory Health and Safety Group.

15 References

Jenkins, R., *X-ray Fluorescence Spectroscopy*, Wiley Interscience, New York 1988

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Margui, E. and Van Grieken, R., *X-Ray Fluorescence Spectrometry and Related Techniques*, Momentum Press LLC, New York 2013

Chemistry Unit Quality Assurance and Operations Manual, Federal Bureau of Investigation, Laboratory Division, latest revision

Operation of the Thermo QUANT'X X-Ray Fluorescence Spectrometer, Metallurgy Manual 501, Chemistry Unit, latest revision

Operation of the Bruker M4 Tornado X-Ray Fluorescence Spectrometer, Metallurgy Manual 502, Chemistry Unit, latest revision

Operation of the Olympus Delta Handheld X-Ray Fluorescence Spectrometer, Metallurgy Manual 503, Chemistry Unit, latest revision

Examinations for Association or Origin, Metallurgy Manual 100, Chemistry Unit, latest revision

Rev. #	Issue Date	History
1	03/02/2018	Renumbered Metallurgy SOP Manual documents. This document was formerly Metal 25 and is now designated Metal 500. Included referenced acronym in title. Added personnel to section 2. Made minor editorial corrections and terminology changes throughout document. Deleted obsolete equipment in section 5. Incorporated section 7 into section 6 and renumbered subsequent sections. Added requirement for sampling plan retention in section 7. Added section 8.1.e to clarify operation. Revised description of instrument performance check in section 10.1. Updated section 13 to clarify instrument limitations. Deleted obsolete section 14.c. Added additional references to section 15.
2	08/16/2021	Edited Scope to include polymeric exams. Minor grammatical edits throughout. Changed “sample” to “specimen”, “substance”, or “material” as appropriate. Clarified language in Standards and Controls, Sampling, and Decision Criteria sections. Added specific instrument SOP references. Provided for detectors with windows other than beryllium in Limitations and Safety sections. Differentiated the application of CRMs v. reference materials in the Equipment section. Removed overt references to FBI Laboratory over-arching quality documents.

Approval

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